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Spin-orbit coupling parameters and electron g factor of II-VI zinc-blende materials

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We perform tight-binding estimates and linear muffin-tin-orbital calculations of the Δ_0, Δ_0', and Δ^- spin-orbit coupling parameters of II-VI zinc-blende materials. Good agreement is found in the case of ZnTe with recent experimental results by Drechsler *et al.* [Phys. Rev. B **50**, 2649 (1994)]. The contribution from the Δ^- parameter to the electron g factor of II-VI materials is calculated and found to be larger than the "conventional" g factor (without the Δ^- contribution) in the case of ZnTe, but smaller for the other II-VI compounds. From the momentum matrix elements used in the calculations, realistic values of the Luttinger parameters are estimated.

I. INTRODUCTION

A recent paper by Drechsler *et al.*[1] addressed the nonparabolicity, anisotropy, and spin splitting of the conduction band of the II-VI semiconductor ZnTe. These results were satisfactorily described by theoretical calculations based on a 14 × 14 $\vec{k}\cdot\vec{p}$ model.[2] Furthermore, a fit to the experimental spin-splitting data leads to an off-diagonal spin-orbit coupling parameter: $\Delta^- = -0.33$ eV. To the authors' knowledge, this is the only value of Δ^- reported for II-VI zinc-blende semiconductors.

In this Brief Report, we obtain values of the Δ^- parameter and the spin-orbit splittings Δ_0, Δ_0' in the II-VI zinc-blende semiconductors: ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, and HgTe, based on tight-binding estimates and first-principles linear muffin-tin-orbital (LMTO) calculations.[9] The Δ^- parameter is known to affect spin splittings and the electron g factor.[3] Following the determination of spin-orbit coupling parameters, we estimate the electron g factor of the abovementioned materials (including the contribution from the Δ^- parameter) and compare our results with the "conventional" g factor (without the Δ^- contribution).

The off-diagonal spin-orbit coupling parameter Δ^- is defined as

$$\Delta^- = 3\left\langle \left(\frac{3}{2}\frac{3}{2}\right)_v \middle| H_{\rm so} \middle| \left(\frac{3}{2}\frac{3}{2}\right)_c \right\rangle , \tag{1}$$

where $|\left(\frac{3}{2}\frac{3}{2}\right)_v\rangle$ ($|\left(\frac{3}{2}\frac{3}{2}\right)_c\rangle$) represents the eigenvectors of the corresponding valence (conduction) states, and $H_{\rm so}$ is the spin-orbit Hamiltonian. According to the usual phase convention,[3,4] Δ^- is real. If we assume that the Γ_{15}^v and Γ_{15}^c wave functions are obtained as bonding and antibonding linear combinations of the anion ($|\,\mathrm{VI}\,\rangle$) and cation ($|\,\mathrm{II}\,\rangle$) p states, we have

$$\begin{aligned} |\,\Gamma_{15}^v\rangle &= \alpha\,|\,\mathrm{VI}\rangle + \beta\,|\,\mathrm{II}\rangle, \\ |\,\Gamma_{15}^c\rangle &= \beta\,|\,\mathrm{VI}\rangle - \alpha\,|\,\mathrm{II}\rangle . \end{aligned} \tag{2}$$

Again, following the phase conventions of Refs. 3 and 4: $\alpha > 0$ and $\beta < 0$. It is now possible to write down explicit expressions of the spin-orbit splittings Δ^-, Δ_0, and Δ_0' by taking off- and on-diagonal matrix elements of the spin-orbit Hamiltonian $H_{\rm so}$ in the basis states of Eq. (2).[3] As a result, we find

$$\begin{aligned} \Delta^- &= \alpha\beta\,[\Delta(\mathrm{VI}) - \Delta(\mathrm{II})] , \\ \Delta_0 &= \alpha^2\Delta(\mathrm{VI}) + \beta^2\Delta(\mathrm{II}) , \\ \Delta_0' &= \beta^2\Delta(\mathrm{VI}) + \alpha^2\Delta(\mathrm{II}) , \end{aligned} \tag{3}$$

where $\Delta(\mathrm{VI})$ and $\Delta(\mathrm{II})$ are the atomic spin-orbit splittings properly renormalized to take into account the compression of the atomic wave function in the core and the fact that the states near the top of the valence bands are not completely p-like, but have a considerable admixture of d (and higher angular momentum) components.[5] The normalization factor is about 1.5 in diamond and zinc-blende crystals. The parameters α and β in (2) and (3) can be obtained from the relations $\alpha^2 + \beta^2 = 1$ and[6]

$$\frac{\alpha}{\beta} = \frac{-2H_{xx}}{E_p^{\mathrm{VI}} - E_p^{\mathrm{II}} + \left[(E_p^{\mathrm{VI}} - E_p^{\mathrm{II}})^2 + 4H_{xx}^2\right]^{1/2}} , \tag{4}$$

where E_p^{VI} and E_p^{II} are the atomic term values that appear on the diagonal of the tight-binding Hamiltonian, see Table 2.2 in Ref. 6. H_{xx}, a nearest-neighbor matrix element between p states, is a function of the bond length d and can be written as[6,7]

$$H_{xx} = \frac{4}{3}V_{pp\sigma} + \frac{8}{3}V_{pp\pi} = \frac{1.28}{d^2} \tag{5}$$

in atomic units. This equation is based on parameters derived within an orthogonal nearest neighbor sp^3s^* tight-binding model. From the values of $\Delta(\mathrm{VI})$ and $\Delta(\mathrm{II})$ listed in Refs. 5 and 8, we obtain the values of Δ^- listed in Table I. Note, in particular, the satisfactory agreement of $\Delta^- = -0.28$ eV found here with the result given by Drechsler *et al.*: $\Delta^- = -0.33$ eV. We also observe from Table I that the off-diagonal spin-orbit contribution Δ^- is considerably higher for the II-VI compounds with Te

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TABLE I. Spin-orbit coupling parameters Δ^-, Δ_0, and Δ_0' (in eV) calculated by various procedures (see footnotes) for different zinc-blende II-VI semiconductors.

	$\Delta^{-\text{a}}$	$\Delta_0{}^{\text{a}}$	$\Delta_0'{}^{\text{a}}$	$\Delta^{-\text{b}}$	$\Delta_0{}^{\text{b}}$	$\Delta_0'{}^{\text{b}}$	$\Delta^{-\text{c}}$	$\Delta_0{}^{\text{c}}$	$\Delta_0'{}^{\text{c}}$
ZnS	0.00	0.074	0.074				0.012	0.10	0.15
ZnSe	−0.052	0.47	0.081	−0.046	0.42	0.070	−0.040	0.45	0.15
ZnTe	−0.28	1.02	0.15				−0.26	0.95	0.15
CdS	0.027	0.079	0.22						
CdSe	−0.047	0.47	0.24						
CdTe	−0.19	1.06	0.27	−0.16	0.93	0.29	−0.14	0.95	0.36
HgS	0.084	0.11	0.48						
HgSe	0.004	0.48	0.50						
HgTe	−0.12	1.07	0.53	−0.12	0.90	0.38			

[a] Obtained from renormalized atomic splittings of Refs. 5 and 8 (present work).

[b] Δ_0 and Δ_0' obtained with the LMTO method and corresponding value of Δ^- determined from these Δ_0 and Δ_0' with the tight-binding method (present work).

[c] Δ_0 and Δ_0' obtained with the ROPW method (Ref. 10) and corresponding value of Δ^- determined here from these Δ_0 and Δ_0' with the tight-binding method.

as the anion compared to the other II-VI materials. This is a consequence of the large spin-orbit splitting in Te:[5] renormalized $\Delta(\text{Te})=1.10$ eV. In columns 3 and 4 of Table I, we give the Δ_0 and Δ_0' spin-orbit splittings found using Eq. (3). Finally, we show in Table I (columns 5–10) the results for the spin-orbit splittings Δ_0, Δ_0', and Δ^- of some II-VI compounds, obtained with the linear muffin-tin-orbital (LMTO) band structure method and relativistic orthogonal plane wave (ROPW) results given by Wepfer *et al.*[10] The Δ^- values are derived from the Δ_0 and Δ_0' splittings found with the LMTO method and in Ref. 10, respectively, using the tight-binding relations of Eq. (3) for the spin-orbit splittings of the constituent ions. In general, we find good agreement among the different methods, indicating that the simple tight-binding method give good estimates (columns 2–4 in Table I).

We now discuss the electron g factors of the compounds. Based on $\vec{k}\cdot\vec{p}$ perturbation theory, the following expression is derived:[11,12]

$$\begin{aligned} g - g_0 &= \frac{2}{im_0} \sum_n \frac{\langle S \mid p_x \mid n\rangle\langle n \mid p_y \mid S\rangle - \langle S \mid p_y \mid n\rangle\langle n \mid p_x \mid S\rangle}{E(\Gamma_1^c) - E_n} \\ &\approx -\frac{4P^2}{3}\left(\frac{1}{E_0} - \frac{1}{E_0 + \Delta_0}\right) - \frac{4P'^2}{3}\left(\frac{-1}{E(\Gamma_8^c) - E_0} + \frac{1}{E(\Gamma_7^c) - E_0}\right) + 2C' , \end{aligned} \tag{6}$$

TABLE II. Momentum matrix elements P, P', Q, in atomic units, and the corresponding Luttinger parameters γ_1, γ_2, γ_3. In the evaluation of the Luttinger parameters, we have approximated Q for the different II-VI compounds by averaging over the corresponding isoelectronic group IV materials. In the case of CdS and CdSe, due to the lack of experimental data, we used the P and P' values of ZnS and ZnSe, respectively.

	P	P'	Q	γ_1	γ_2	γ_3
ZnS	0.676,[a] 0.530 [b]	0.621,[a] 0.351[b]	0.574	2.12,[a] 1.28[b]	0.51,[a] 0.09[b]	1.56,[a] 1.14[b]
ZnSe	0.668[b]	0.425[b]	0.607	3.21[b]	0.75[b]	2.00[b]
ZnTe	0.601[a]	0.124[a]	0.553	3.44[a]	0.59[a]	2.03[a]
CdS	0.676,[a] 0.530[b]	0.621,[a] 0.351[b]	0.607	3.44,[a] 2.20[b]	0.97,[a] 0.35[b]	2.15,[a] 1.53[b]
CdSe	0.668[b]	0.425[b]	0.553	4.40[b]	1.60[b]	2.68[b]
CdTe	0.622[a]	0.306[a]	0.494	4.34[a]	1.60[a]	2.66[a]
HgS	0.585[c]	0.428[d]	0.553	−41.8[d]	−21.2[d]	−20.7[d]
HgSe	0.493[e]	0.332[e]	0.494	−18.6[e]	−9.71[e]	−9.10[e]
HgTe	0.566[f]	0.372[f]	0.494	−14.1[f]	−11.5[f]	−8.19[f]

[a] From the electron effective mass and the P of Ref. 19.

[b] From the relationship between P and P' given in Eq. (2.3) of Ref. 3, and the electron effective mass.

[c] From Ref. 19, which assumes that the E_0 gap of zinc-blende HgS is ~ -0.15 eV. See also Ref. 20.

[d] From the relationship between P and P' given in Eq. (2.3) of Ref. 3, and the P of Ref. 19.

[e] From the values of P given in Ref. 17, and Eq. (2.3) of Ref. 3.

[f] From the effective mass of the Γ_6 (valence) band, and Eq. (2.3) of Ref. 3.

where g_0 is the free-electron g factor, P (P') is the matrix element of p_x between Γ_1^c and Γ_{15}^v (Γ_{15}^c), and C' is approximately -0.02 in all compounds[12,13] and supposedly accounts for contributions to g from remote bands. However, experimental results by Chen *et al.*[14] revealed that the above expression for g is inadequate. In order to obtain good agreement with experiment, one must include a contribution Δg to the electron g factor related to Δ^-. This third-order perturbation expression involves twice $\vec{k}\cdot\vec{p}$ matrix elements and once $H_{\rm so}$ (Δ^-), following[15]

$$\Delta g = \frac{8}{9}\frac{\Delta^- P P'}{E(\Gamma_7^c) - E(\Gamma_8^v)}\left[\frac{1}{E_0}+\frac{2}{E_0+\Delta_0}\right]. \qquad (7)$$

In the III-V semiconductor InSb, e.g., this contribution amounts to -1.7 and plays an important role in the magnetic field dependence of the spin splitting.[15,16] In Table II, we list the momentum matrix elements: P, P', and $Q = i\langle \Gamma_{15,x}^v \mid p_y \mid \Gamma_{15,z}^c\rangle$, and the corresponding Luttinger parameters γ_1, γ_2, γ_3. We have approximated Q for the different II-VI compounds by averaging those of the corresponding isoelectronic group IV materials as obtained from their γ_i's (Ref. 17 for Si and Ge, Ref. 18 for α-Sn). In Table III, we show the values of Δg and the total g factor ($g+\Delta g$) for the different II-VI compounds, as calculated from the Δ's of Table I (columns 2–4), and the P and P' parameters of Table II. It is found that the absolute value of Δg (column 2 in Table III) is larger than the total g factor (column 3 in Table III) for ZnTe, but smaller for the other II-VI compounds. Due to the lack of experimental and theoretical information about P and P' in CdS and CdSe, their g's were obtained using the P and P' values of ZnS and ZnSe, respectively. This should be a good approximation since P and P' are almost independent of material combination within the III-V family and are expected to be so also for the II-VI zinc-blende type materials.[19]

TABLE III. Δg contribution of the off-diagonal spin-orbit coupling parameter Δ^- to the electron g factor [Eq. (7)] and the total g factor given by $g+\Delta g$, where g has been obtained from Eqs. (6) and (7). For comparison, we also list experimental values found in Ref. 17.

	Δg	$g+\Delta g$	Exp.
ZnS	0.00	1.87,[a] 1.94[b]	1.885
ZnSe	−0.08[b]	1.19[b]	1.15
ZnTe	−0.51[a]	−0.30[a]	−0.40
CdS	0.06,[a] 0.03[b]	1.78,[a] 1.89[b]	1.75[c]
CdSe	−0.08[b]	0.23[b]	0.54[c]
CdTe	−0.33[a]	−1.64[a]	−1.59
HgS	−1.65[d]	−72.2[d]	
HgSe	0.013[e]	80.5[e]	
HgTe	0.22[f]	56.1[f]	41

[a] Values of P and P' given in (a), Table II.

[b] Values of P and P' given in (b), Table II.

[c] Measured for the wurtzite modification. Here, the average $(g_\parallel + 2g_\perp)/3$ is given.

[d] Values of P and P' given in (c) and (d), respectively, Table II.

[e] Values of P and P' given in (e), Table II.

[f] Values of P and P' given in (f), Table II.

In conclusion, we have performed tight-binding estimates and LMTO calculations of the Δ^-, Δ_0, and Δ_0' spin splittings in zinc-blende type II-VI semiconductors. In particular, the Δ^- value of ZnTe ($\Delta^- = -0.28$ eV) is found to be in reasonable agreement with the value obtained by Drechsler *et al.* ($\Delta^- = -0.33$ eV). To the authors knowledge, the value of Δ^- given by Drechsler *et al.* is the only value for Δ^- reported so far for II-VI compounds. Finally, we have calculated the contribution of Δ^- to the electron g factor and found it to be larger in magnitude than the "conventional" g factor (g calculated without the Δ^- contribution) for ZnTe, but smaller for the other II-VI crystals. From the values of P and P' used here, and a reasonable estimate of Q, we have calculated the Luttinger parameters γ_i of the zinc-blende type II-VI compounds. In view of the scarcity and unreliability of existing experimental data, these values of γ_i provide a realistic estimate.

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